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(54) Title: ETHYLENE POLYMER PRODUCT HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION, ITS PREPARATION AND USE

(57) Abstract

Although ethylene polymer products having a bimodal or multimodal molecular weight distribution have good processability and mechanical properties, these properties are not entirely satisfactory. Such bimodal or multimodal ethylene polymer products are now being improved by (a) forming a blend of a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and at least a second ethylene polymer having a second average molecular weight which is higher than said first average molecular weight and a second molecular weight distribution giving the blend a third average molecular weight and a third molecular weight distribution which is at least bimodal, (b) heating and melt processing the blend of step (a) into a molten ethylene polymer having a fourth average molecular weight and a fourth molecular weight distribution, and (c) cooling and solidifying the molten ethylene polymer into said ethylene polymer product, whereby in step (b), the blend of step (a) is subjected to controlled free radical reactions in such a way that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight, and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.

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ETHYLENE POLYMER PRODUCT HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION, ITS PREPARATION AND USE

The invention relates to a process for the preparation of a solid ethylene polymer product, containing from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α-olefin and having a broad molecular weight distribution.

In certain applications, where films, bottles, cables and pipes are produced by extrusion or blow molding, the ethylene polymers having narrow molecular weight distribution are not satisfactory, because of the poor melt flow properties and poor processability. Therefore, different approaches have been suggested for manufacturing polyethylenes having a broad molecular weight distribution. One approach to widen the molecular weight distribution is to blend a low molecular weight ethylene polymer with a high molecular weight ethylene polymer either mechanically or in solution. More than two ethylene polymers having different molecular weights can also be mixed together.

Attempts have been made to broaden molecular weight distribution by a proper selection of catalysts.

There are also known various multi-stage processes for broadening the molecular weight distribution by carrying out the polymerization using different hydrogen and co-monomer concentrations in each stage.

US 5,326,835 discloses a multi-stage process for producing ethylene polymer having a bimodal and/or broad molecular weight distribution in a multi-step reaction sequence. According to this patent, the first reaction step is performed in a loop reactor and one or more subsequent steps are performed in one or more gas phase reactors. The molecular weight distribution can be controlled by using different concentrations of hydrogen chain transfer agent and co-monomer in different steps.

By bimodal and multimodal distribution is generally and in connection with the present invention meant a broad molecular weight distribution produced by blending two or more polymer components with different molecular weights or by polymerizing to different molecular weights in a process with two or more reactors in series. Unimodal distribution is obtained with essentially only one molecular weight fraction.

In spite of the methods for broadening the molecular weight disclosed above, the ethylene polymers produced up till now have not had entirely satisfactory properties. This applies for the processability properties in general, and for the melt strength of the unloaded polymer melt during processing in particular. The latter property is important eg. for bubble stability during film blowing and controlled orientation during extrusion, especially the extrusion of ethylene polymer film.

The aim of the invention is to produce an ethylene polymer product having both better processability and melt strength. Especially, the ethylene polymer product should have low melt viscosity under high shearing forces and high melt viscosity under low shearing forces.

The exposing of polyolefins to severe conditions such as reactive chemicals and/or high temperature is known to induce a wide range of the free radical reactions. Thus the patents US 3,551,943; US 3,563,972; US 3,608,001; and US 3,898,209 disclose a controlled rheology process for polypropylene that involve the extrusion of polypropylene in the presence of air. Under such conditions the molecular weight of polypropylene is lowered by degradation and at the same time the molecular weight distribution is narrowed. The molecular weight of unimodal polyethylene was increased by reactive peroxide treatment in Lachtermacher, M., Rudin, A., J. Appl. Polym. Sci., Vol. 59 (1996) 1213-1221.

EP 0 700 769 discloses the treatment of polyethylene with a broad molecular weight distribution using oxygen or oxygen containing gas. The feeding of oxygen into a melt porcessing apparatus is uncontrollable and does not result in broadened molecular weight distribution. See page 6, lines 15 and 16 of said EP application. The oxidized polyethylene is preferentially prepared by chromium oxide catalyst.

The present invention has now succeeded in improving an ethylene polymer product for better processability, melt strength and orientation. In the claimed process, an ethylene polymer product is produced, which contains from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α-olefins and has a broad molecular weight distribution. In the process:

(a) a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and at least a second ethylene polymer having a second average molecular weight which is higher than said first average molecular weight, and a second molecular weight distribution are formed into a blend having a

third average molecular weight and a third molecular weight distribution which is at least bimodal;

(b) the blend of step (a) is heated and melt processed into a molten ethylene polymer having a fourth average molecular weight and fourth molecular weight distribution;

a stabilizer is optionally added in step (b), and

(c) the molten ethylene polymer is cooled and solidified into said ethylene polymer product.

The process according to the invention is substantially characterized in that in the above step (b), the blend of step (a) is subjected to controlled free radical reactions so that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight, and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.

The average molecular weights and the molecular weight distributions can be measured and expressed by any conventional method applied to ethylene polymers products. In this connection, it is convenient that the average molecular weights are measured and expressed as melt flow rates MFR^{i}_{m}, where i refers to the first, second, third and fourth average molecular weight and m refers to the load of the piston used for measuring the MFRs, which load in the following examples generally is 5.0 kg (ISO 1133), the molecular weight distributions are expressed as the flow rate ratios, $FRR^{i}_{m1/m2}$, i.e. the ratios between high load MFR^{i}s and low load MFR^{i}s, where i refers to the first, second, third and fourth molecular weight distribution, and m^{1} and m^{2} refer to the high load, generally 21.6 kg, and low load, generally 5.0 kg or 2.16 kg, respectively.

By Melt Flow Rate (MFR) is meant the weight of a polymer pressed through a standard cylindrical die at a standard temperature in a laboratory rheometer carrying a standard piston and load. Thus MFR is a measure of the melt viscosity of a polymer and hence also of its molecular weight. The smaller the MFR, the larger is the molecular weight. It is frequently used for characterizing a polyolefin, especially polyethylene, when the standard conditions MFR_{m} are: temperature 190°C; die dimensions 9.00 cm in length and 2.095 cm in diameter; load of the piston, 2.16 kg (m=2), 5.0 kg (m=5), 10.0 kg (m=10), 21.6 kg (m=21). See Alger, M.S.M., Polymer Science Dictionary, Elsevier 1990, p. 257.

By Flow Rate Ratio ($FRR_{m1/m2}$) is meant the ratio between the melt flow rate (MFR_{m1}) measured at a standard temperature and with standard die dimensions using a heavy load ($_{m1}$)and the melt flow rate (MFR_{m2}) measured at the same temperature with the same die dimensions using a light load ($_{m2}$). Usually, for ethylene polymers, the heavy load m^1 is 21.6 kg and the light load m^2 is 5.0 kg or 2.16 kg (ISO 1133). The larger the value of the $FRR_{m1/m2}$, the broader is the molecular weight distribution.

In step (b) of the claimed process the blend of step (a) is heated, melt processed into a molten ethylene polymer, and subjected to free radical reactions.

The melt processing equipment for step (b) can be any suitable heated machine which melts the blend of step (a) and exerts shearing forces upon the blend. Such machines are e.g. extruders, calanders, kneaders, mixers, etc., preferentially extruders. The free radicals inducing reagent can be introduced to any part of the machine such as the feed zone, melting zone and/or conveying zone of an extruder. The preferred mechanical energy of the machine is 100 to 500 kWh per g of polymer blend.

The blend of step (a) is subjected to free radical reactions to such an extent that the relative MFR_5 decreases, that is $-(MFR^4{}_5 - MFR^3{}_5):MFR^3{}_5$, is from 5 to 100%, preferentially from 10 to 80%. The upper limit is not to be interpreted as a limitation, but it has only a descriptive function, which is based on the experimental results obtained in connection with the present invention. Anyhow, it appears that the melt viscosity increases by several tens of per cent, which means that the controlled radical essentially lead to the combination of radical fragments into larger ethylene polymer molecules than before the free radical reactions. Indeed, it was very surprising that the subjection of an ethylene polymer having a bimodal or multimodal distribution to free radical reactions would lead to an increase of the molecular weight and thus to an increase in the melt strength and the mechanical properties of the product.

In step (b) of the claimed process, the blend of step (a) is preferentially subjected to controlled free radical reactions so that the relative broadening (increase) of the molecular weight distribution expressed as $+(FRR^4{}_{21/5} - FRR^3{}_{21/5}):FRR^3{}_{21/5}$ is from 5 to 100%, most preferentially from 10 to 80%. It was also extremely surprising that the molecular weight distribution would be broadened by free radical reactions, since the above mentioned controlled rheology process for polypropylene

led to a narrowing of the molecular weight distribution and the oxygenation of polyethylene did not influence it. The upper limit of the disclosed flow rate ratios are not to be interpreted as limiting the scope of protection, but is only based on the embodiment of the examples.

The most important feature of the heating and melt processing step (b) is the occurance of controlled free radical reactions. Free radical reactions can be effected in many ways. Firstly, free radicals may be generated from initiators in diverse ways, among which thermal or photochemical intermolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the most common, but other processes such as the use of γ-radiation or electron beams find application. Free radicals can also be generated by means of reaction of the ethylene polymer blend by means of thermal decomposition with or without the presence of oxygen. Thermal treatment is a suitable method, especially if unstabilized polyethylene is used or if the used ethylene polymer is destabilized during the treatment.

Among decomposable thermal initiators, the following can be mentioned: azo-compounds such as azobisisobutyronitrile (AIBN), peroxy compound such as diacyl peroxides, acetyl alkylsulfonyl peroxides, dialkyl peroxydicarbonates, *tert*-alkylperoxyesters, *OO-tert*-alkyl *O*-alkyl monoperoxycarbonates, di(*tert*-alkylperoxy)-ketals, di(*tert*-alkyl)peroxides, *tert*-alkyl hydroperoxides, and ketone peroxides, redox initiators, etc. According to one embodiment of the invention, the half life of the thermal initiators used during 10 h is from 38 to 172°C, preferentially from 54 to 128°C.

Especially preferential are peroxy compounds of which the following can be mentioned: diacylperoxides, such as dibenzoyl peroxide BPO, di(2,4-dichlorobenzoyl) peroxide, diacetyl peroxide, dilauroyl peroxide, didecanoyl peroxide, diisononanoyl peroxide and succinic acid peroxide; commercial peroxy esters, such as di-*tert*-butyl diperoxyphthalate, *tert*-butyl perbenzoate, *tert*-butyl peracetate, *tert*-amyl perbenzoate, 2,5-di(benzoylperoxy)-2,5-dimethylhexane, *tert*-butyl peroxymaleic acid, *tert*-butyl peroxyisobutyrate, *tert*-butyl peroxy-2-ethylhexanoate(*tert*-butyl peroctoate), *tert*-amyl peroctoate, 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane, *tert*-butyl peroxypivalate, *tert*-amyl peroxypivalate, *tert*-butyl peroxyneodecanoate, *tert*-amyl peroxyneodecanoate, α-cumyl peroxyneodecanoate; diperoxyketals, such as ethyl-3,3-di(*tert*-butylperoxy)butyrate, ethyl 3,3-di(*tert*-amylperoxy)-butyrate, *n*-butyl 4,4,-di(*tert*-butylperoxy)valerate, 2,2-di(*tert*-butylperoxy)butane, 1,1-di(*tert*-butylperoxy)cyclohexane, 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclo-

hexane, and 1,1-di(*tert*-amylperoxy)cyclohexane; dialkylperoxides, such as 2,5-(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne, di-*tert*-butyl peroxide, *tert*-butyl-α-cumyl peroxide, 2,5-di(*tert*-butylperoxy)-2,5-dimethylhexane, α-α'-di(*tert*-butylperoxy)-1,3- and 1,4-diisopropylbenzene, and dicumylperoxide; peroxydicarbonates such as di-*n*-propyl peroxydicarbonate, diisopropyl peroxycarbonate, dicetyl peroxydicarbonate, di-*sec*-butyl peroxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, and di(4-*tert*-butylcyclohexyl)peroxydicarbonate; and *tert*-alkylhydroperoxides such as *tert*-butyl hydroperoxide, *tert*-amyl hydroperoxide, cumene hydroperoxide, 2,5-dihydroxyperoxy-2,5-dimethylhexane, pinane hydroperoxide, *para*-menthane hydroperoxide, and diisopropylbenzene hydroperoxide.

Preferred peroxy initiators are chosen from: 2,5-dimethyl-2,5-di(*tert*- butylperoxy)hexyne-3; 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane; di-*tert*-butyl peroxide; di-*tert*-butylperoxyisopropyl benzene; *tert*-butylcumylperoxide; dicumylperoxide; 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetracyclononane; 4,4-di-*tert*-butyl peroxy-n-butylvalerate; 1,1-di-*tert*-butyl peroxycyclohexane; *tert*-butyl peroxybenzoate; dibenzoyl peroxide; di(2,4-dichlorobenzoyl)peroxide; di(p-chlorobenzoyl) peroxide; 2,2-di(*tert*-butylperoxy)butane; ethyl-3,3-bis(*tert*- butylperoxy) butyrate. Most preferred are 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and bis(*tert*-butylperoxyisopropyl)-benzene.

In the invention it is clear that several parameters influence the generation of radicals. For example, if the initiator decomposes easily into radicals, a lower temperature and/or shorter time is needed for radical generation. If the temperature is higher, then generally a shorter time and/or a less reactive initiator is needed for radical generation. Thus, provided with the inventive concept, it is clear for the skilled person, that the radical generation can be controlled experimentally with normal work and without inventive skill. What the skilled person did not know was that it was possible to increase the molecular weight and broaden the molecular weight distribution thus improving the melt strength and mechanical properties of bi- and multimodal ethylene polymers by controlled free radical reactions during melt processing. Uncontrolled free radical treatment leads to decomposition and smaller molecular weight polymer. Oxygenation leads to crosslinking and unchanged molecular weight and distribution thereof.

In the case where thermally decomposing initiators are used, the heating and melt processing of step (b) is preferentially carried out at 180°C to 290°C, most preferentially from 200°C to 270°C.

The amount of generated radicals is naturally also dependent on the amount of initiators added to step (b) of the claimed process. In step (b) the preferential initial content of initiator or optionally content of initiator left after reaction with an added stabilizer, is from 20 ppm to 2000 ppm, most preferentially from 50 ppm to 500 ppm, calculated on the weight of the blend of step (a). Later in step (b), of course, the content of initiator decreases as it decomposes into radicals.

As was mentioned above, the average heating and melt processing time in step (b) of the claimed process has much influence on the generation of free radicals. Depending on the other parameters used, it can vary very much. When using radical initiators, the average heating and melt processing time in step (b) is preferentially from 0.1 min to 30 min and most preferentially from 0.5 min to 10 min.

In the embodiment disclosed above, the blend of step (a) is subjected to free radical reactions by means of free radical initiators. However, there is a second very suitable process for inducing radical reactions. Radical reactions can namely be induced merely by heating the polymer during step (b). In such a step of thermal treatment, the temperature is preferentially from 220°C to 320°C, most preferentially from 240°C to 300°C. In such a case, the average heating and melt processing time in step (b) is from 0.1 min to 30 min, preferentially from 0.5 min to 10 min.

When generating radicals by means of thermal treatment, it is preferable to use an essentially unstabilized or lightly stabilized blend of step (a) as raw material for step (b) of the claimed process.

In order to stabilize the final ethylene polymer product, a stabilizer can be added at the end of step (b), after the needed amount of radical reactions have taken place. It is then added to and mixed with the molten ethylene polymer.

In the following, stabilizers for controlled radical treatment and/or final stabilization are disclosed. All polymeric materials undergo oxidation which can occur in every stage of the life cycle of the polymer (processing, storage, end-use (ageing, weathering)). The reaction is initiated by heat, light, mechanical stress (shear), catalyst residues, impurities etc. and yields alkyl radicals (R·). The generated free radicals can lead to a degradation of the polymer:

Initiation:
RH (polymer) → R· (alkyl radical)

Propagation:
R· + O_2 → ROO· (peroxy radical),
ROO· + RH →·ROOH (hydroperoxide) + R·

Stabilizers (antioxidants, UV stabilizers and metal deactivators) interrupt the degradation in different ways according to their structure.

The antioxidants protect polyolefins against oxidation by controlling molecular weight changes leading to loss of physical and mechanical properties. Commonly the antioxidants are divided in two groups (primary and secondary antioxidants) according to their function in the polymer.

The primary antioxidants (AH) react rapidly with the peroxy radicals and stop the chainbreaking by forming hydroperoxides and stable antioxidant radicals (A·):

ROO· + AH (antioxidant) → ROOH (hydroperoxide) + A·

This (A·) can react further and be regenerated by heat or light:

R· + A· → RA and regeneration → AH

The majority of primary antioxidant for polyolefins are sterically hindered phenols which protect the polymer during processing and improve thermal stability and give long term protection.

The secondary antioxidants reduce the unstable hydroperoxides to inert products. In combinations with primary antioxidants they give added stability to the polymer (synergism).

The most popular secondary antioxidants are the phosphites, phosphonites and the thioethers. These are so called process stabilizers and the phosphites are the most effective during processing and protect both the polymer and the primary anti-oxidant (reduce discolouration). Hydrolytically stable phosphites are mainly used.

Thioethers are useful only in increasing the long-term heat stability performance of phenolic antioxidants. They can provide cost savings by reducing the level of primary antioxidants.

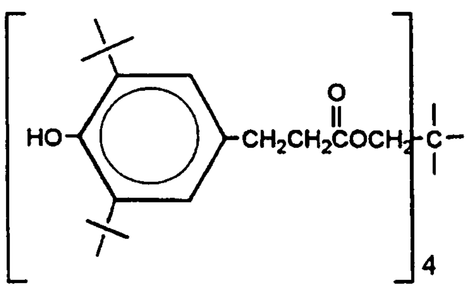
The main antioxidants for polyolefins are often referred to the Ciba-Geigy's Irganox and Irgafos trademarks (also by their competitors). The chemical structures of the antioxidants are viewed in the Table below.

Table

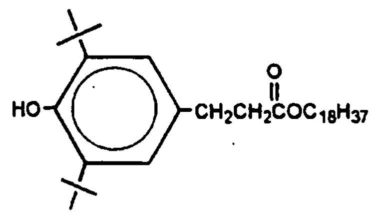
Antioxidants for polyolefins: chemical structures

Sterically hindered phenols:

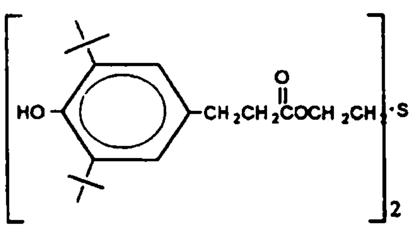
Irganox 1010



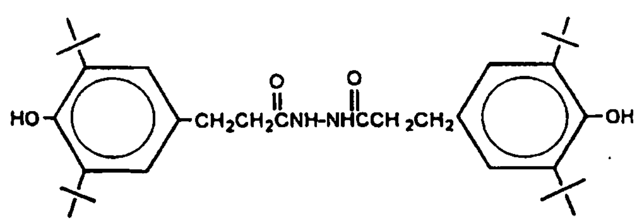
Irganox 1076



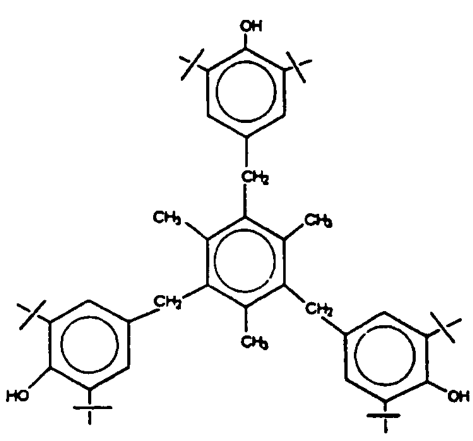
Irganox 1035



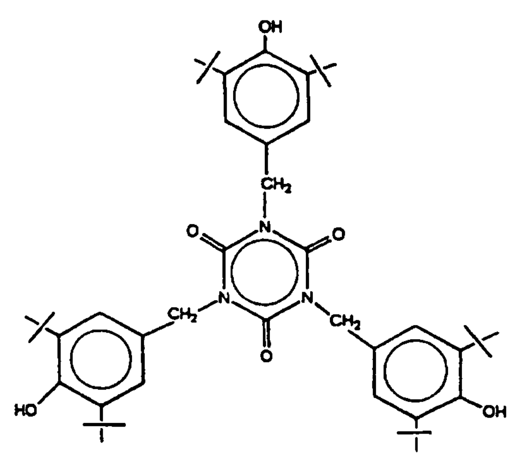
Metal deactivator
Irganox MD 1024



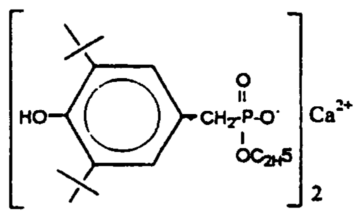
Irganox 1330



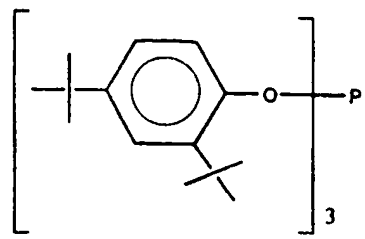
Irganox 3114



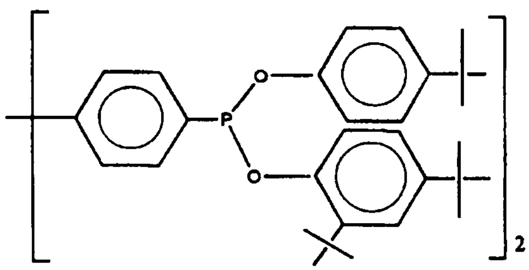
Irganox 1425 WL



Phosphite
Irganox 168



Phosphonite
Irgafos P-EPQ



Thioethers:

Irganox PS 800

$CH_2CH_2COOC_{12}H_{25}$
|
S
|
$CH_2CH_2COOC_{12}H_{25}$

Irganox PS 802

$CH_2CH_2COOC_{18}H_{37}$
|
S
|
$CH_2CH_2COOC_{18}H_{37}$

UV stabilizers protect the polymer from the degradative attack of UV energy in outdoor applications. The UV stabilizers used in polyolefins are classified according to their function in screeners, absorbers and free-radical scavengers.

The screeners are pigments absorbing or reflecting UV light. Carbon black and titanium dioxide are the most used.

UV absorbers are aromatic compounds which can absorb the UV energy and convert it into heat. They are effective in thick sections.

The free-radical scavengers inhibit the propagation through a combination of scavenging and terminating free radicals and decomposing hydroperoxides to harmless products. The hindered amine light stabilizers (HALS) belong to this group of UV stabilizers.

More specifically, it is dependently of the antioxidant fed, preferential in step (b) to add from 0 to 500 ppm of a first stabilizer to the blend of step (a) essentially at the beginning of step (b) and to add from 400 to 1400 ppm of a second stabilizer to the molten ethylene polymer essentially at the end of step (b), the first and second stabilizers being equal or different. According to a preferred embodiment of adding stabilizers, the first stabilizer added in step (b) is a different stabilizer than the second stabilizer, most preferentially so, that the first stabilizer is a weak process stabilizer allowing radical reactions partially, whereas the second stabilizer is a strong process stabilizer essentially preventing radical reactions during melt processing.

As was indicated in the introduction, the bimodal raw material of the heating, melt processing and controlled free radical treatment of step (b) of the claimed process can be produced by essentially two main process steps, namely the mixing of at least two ethylene polymers having different average molecular weights and by polymerizing in a process having at least two internal steps leading to different molecular weights. If necessary, the two methods can be combined in any suitable way to give the right molecular weight distribution for step (b).

In the following, the mixing in step (a) of a first ethylene polymer and at least a second ethylene polymer is analyzed more closely.

The mixing can be a mechanical mixing of two or more granulates, but is preferentially a melt mixing.

The mixing of step (a) is preferentially a mixing of two molten polymers e.g. by melt processing and compounding equipment such as an extruder.

When feeding the first ethylene polymer to the mixing step (a), the melt flow ratio $MFR^{1}{}_{2}$ of the first ethylene polymer is from 50 to 2000 g/10 min, most preferentially from 100 to 1500 g/10 min. When feeding the second, and optionally the third, etc., polymer to the mixing step (a), their melt flow ratio $MFR^{2,etc.}{}_{21}$ is preferentially from 0.05 to 50 g/10 min. most preferentially from 0.10 to 20/10 min.

During the mixing step (a), the ratio between the first ethylene polymer and the second ethylene polymer is preferentially between 20:80 and 80:20, most preferentially between 20:80 and 60:40.

In its most wide scope, the present invention relates to the molecular weight and its distribution controlling free radical reaction treatment of any bimodal or multimodal ethylene polymer. This also means, that the different ethylene polymers disclosed in step (a) of the present process can have the monomer composition of a homopolymer or a copolymer. Preferentially in step (a), the first ethylene polymer has a C_3-C_{10} α-olefin repeating unit content of 0.0 to 10% by weight, calculated from the weight of the first ethylene polymer.

Usually at least one ethylene polymer component of the blend formed in step (a) is an ethylene copolymer containing a small amount of another olefin. Preferentially, the second ethylene polymer has a C_3-C_{10} α-olefin, preferentially 1-butene, or 1-hexene, repeating unit content from 1.0 to 25% by weight and most preferentially from 2.0 to 15% by weight. When a multimodal blend of step (a) is used instead of a bimodal blend, the further ethylene polymer components can be either homopolymers or copolymers.

Conclusively, in the embodiment where the blend of step (a) is formed by mixing a first ethylene polymer and at least a second polymer, the proportion of the first ethylene polymer and the second, etc., ethylene polymer, the MFR^1 and MFR^2 of said ethylene polymers and the C_3-C_{10} α-olefin repeating unit content of said ethylene polymers are preferentially such that the $MFR^3{}_{21}$ of the blend obtained in step (a) is between 5 and 50 g/10 min, the C_3-C_{10} α-olefin repeating unit content of the blend from step (a) is from 0.2 to 20% by weight, preferentially 0.5 to 15% by weight, and the $FRR^3{}_{21/5}$ is between 10 and 40, most preferentially so that after step (b), the fourth molecular weight distribution is at least bimodal. This means that step (a) is very important when determining the broadness of the molecular weight distribution of the final ethylene polymer product.

The preparation in step (a) of ethylene polymer raw material for the controlled free radical reactions of step (b) by mixing a first, a second, etc. ethylene polymer was disclosed above. Said raw material, i.e. blend of step (a) can also be prepared by performing a multi-step internal polymerization process. In the polymerization process several substeps are performed, in which the first, lower molecular weight ethylene polymer is prepared by polymerizing in a substep (a_1), the second higher

molecular weight ethylene polymer is prepared by polymerizing in a substep (a_2), and optional further ethylene polymers are prepared by polymerizing in optional further substeps, whereby the ethylene polymer of each step is present in the following step.

The polymerization conditions of each substep are such, that ethylene polymers are produced the average molecular weight of which differs so that the end product is bimodal or multimodal. Typically in substep (a_1), a temperature of 40°C to 120°C is used, and, independently, in substep (a_2), a temperature of 60°C to 140°C is used.

The polymerizations are typically insertion polymerizations where Ziegler-Natta or single site polymerization catalyst systems are used. For example in substep (a_1) and/or (a_2), a catalyst system is typically used, which is based on at least a tetra-valent titanium compound as procatalyst and an organoaluminum compound as cocatalyst. When Ziegler-Natta catalyst system are used, procatalyst is preferentially based on titanium tetrachloride $TiCl_4$, magnesium chloride $MgCl_2$, and an optional inert carrier and/or an optional electron donor compound, and a typical cocatalyst is a trialkylaluminum compound. Typical catalysts are e.g. prepared according to WO 91/12182 and WO 95/35323 which are herewith included by reference. A preferential single site polymerization catalyst system is that based on a group 4 (IUPAC 1990) metal metallocene an alumoxane.

When performing a polymerization in step (a), substeps (a_1) and (a_2) can be performed in any order, preferentially so that the catalyst system added to one substep catalyst system is also used in the next and other optional additional substeps.

The most convenient way to regulate the molecular weight during polymerization is to use hydrogen, which acts as a chain-transfer agent by intervening in the insertion step of the polymerization mechanism. Thus it is preferential that in substep (a_1) a hydrogen amount is used, leading to a melt index $MFR^1{}_2$ of the first ethylene polymer of from 50 to 2000 g/10 min., most preferentially from 100 to 1500 g/10 min., when substep (a_1) is performed first.

The properties of the first, second etc. ethylene polymers forming the blend of step (a) also depend on the use of minor amounts of an α-olefin, which is not ethylene. Typically, in substep (a_1), no or a small amount of C_3-C_{10} α-olefin is used, so that the first ethylene polymer has a C_3-C_{10} α-olefin repeating unit content of 0.0 to

10% by weight, of the first ethylene polymer. In the same way, so much C_3-C_{10} α-olefin in substep (a_2) and further optional substeps are used, that at least the second ethylene polymer has a C_3-C_{10} α-olefin, preferentially 1-butene or 1-hexene, repeating unit content of from 1.0 to 25% by weight, preferentially from 2.0 to 15.0% by weight, of at least the second ethylene polymer.

When using only two substeps (a_1) and (a_2) in step (a) of the claimed process, the ratio between the first produced ethylene polymer, having the $MFR^1{}_2$ defined above, and the second produced ethylene polymer, having a lower MFR, is between 20:80 and 80:20, preferentially between 20:80 and 60:40. Thus, it is suitable to use more of the second ethylene polymer than the first ethylene polymer.

The above polymerization conditions of the substeps can be coordinated so that a blend of step (a) is produced, which is most suitable for the melt processing free radical reactions of step (b) and gives a useful final ethylene polymer product.

Accordingly in substeps (a_1) and (a_2) said reaction temperature, catalyst system, portion of C_3-C_{10} α-olefin, amount of hydrogen, and ratio between the first olefin polymer and the second olefin polymer produced are regulated so that $MFR^3{}_{21}$ of the blend of step (a) is between 5 and 50 g/10 min., the C_3-C_{10} α-olefin repeating unit content of the blend of step (a) is from 0.2 to 20% by weight, preferentially from 0.5 to 15.0% by weight, and the FFR^3 defined as $MFR^3{}_{21}/MFR^3{}_5$ is between 10 and 40, preferentially so that after step (b), the fourth molecular weight distribution is at least bimodal, that is, bimodal or multimodal.

The present invention also relates to an ethylene polymer product and preferentially a film material product, which contains from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α-olefin and having a broad molecular weight distribution. The ethylene polymer product is characterized by that it has been prepared by means of the above described process. The ethylene polymer product according to the invention is very processable and has an extraordinary good melt strength. Therefore it is particularly suitable for extrusion applications and especially film blowing, cast-line extrusion, pipe-coating, extrusion coating, as well as in blow moulding applications.

The properties of bimodal and multimodal resins can according to the invention be further improved during compounding step by controlled treating with radical reactions, i.e. by tailoring the molecule structure of the base material. Tailoring is

then based on radical reactions. The reactions can be initiated by peroxides or by using heat and no or a reduced amount of stabilizers in the extruder. The absence or reduced amounts of stabilizers make the controlled peroxide reactions possible in the compounding machine. The tailoring reactions increase the amount of high Mw molecules, which can be seen in the increased zero shear rate viscosity (lower MFR values).

Tailoring during melt compounding gives following improvements without additional process or processing steps:

1. Balanced application properties can be obtained by fine-tuning the tailoring.

2. The elasticity of the ethylene polymer material is increased. This gives better melt strength and processability on film blowing line. Another improvement is a more balanced orientation, which gives better tear strength in the machine direction and thus improves the overall tear strength. Increased elasticity also improves the neck-in and draw down properties on different extrusion applications and gives better stability for the broadness of film on cast-line, pipe coating, extrusion coating etc.

3. The weight swell is an important parameter on blow molding lines. By weight swell is meant the weight of a blow article compared to a reference, using constant parrison length. To have easy processability it has to be adjusted to a suitable level. Tailoring gives a possibility to fine-tune, when necessary, the flow properties and weight swell, which is a function of die swell and sagging. Tailoring decreases die swell and on the other hand the low zero shear rate viscosity obtained results in less sagging and also slower rate of swelling.

In the following, examples are disclosed to illustrate the invention.

EXAMPLES

All the examples are made with materials produced in two or more reactors connected in series.

Example 1

Bimodal polyethene (A) was polymerized with Ziegler-Natta type catalyst prepared according to WO 95/35323 in one loop and one gas phase reactor which are

operated in series. Ethene was polymerized in presence of hydrogen in the loop reactor resulting in MFR_2 = 1030. Ethene was polymerized in presence of 1-butene and hydrogen in the gas phase reactor. The production rate split of reactors was 47% / 53%. The final product MFR_{21} = 10.2 and density 949 kg/m^3. The reaction conditions are presented in Table 1.

The powder from the above polymerization was compounded with different peroxide contents on Werner & Pfleiderer ZSK-30 extruder. The peroxide was 2,5-dimethyl-2,5-di(tert.butylperoxy)-hexane (Luperox 101) and it was added as a master batch in the same powder. The master batch was made in a Papenmeyer mixer. The compounding conditions were 200 rpm, 7 kg/h and Tm = 210°C.

The samples were evaluated by measuring the melt flow and by blowing film on a lab scale Collin G.M.B.H. 30 D extruder. The running conditions on film line were barrel temperature 170° ... 230°, screw speed 50 rpm, output 3.7 kg/h and frost line 300 mm. The diameter of the die was 30.0 mm, die gap 0.75 mm and the diameter of the bubble 95.5 mm, which gives blow up ratio (BUR) = 3.2. The effective blow up ratio (BUReff) means the ratio between the bubble diameter and the narrowest diameter of the film neck. The BUReff value is used to describe elasticity and bubble stability. The higher the BUReff value, the better is the film material.

This example shows, that the bubble stability of bimodal polyolefin material can be improved on film blowing lines by molecular weight tailoring during the compounding process. The results are presented in Table 2.

Table 2

	P1 (comp.)	**P2**	**P3**
Luperox 101 (ppm)	0	100	200
MFR_5	0.37	0.3	0.23
MFR_{21}	10	9.5	8.9
FRR 21/5	27	32	39
Collin (p)	331	326	336
BUReff	3.2	4.3	4.5
FRR incr. %		18.5	44.4
MFR_5 decr. %		19	38

Example 2

Controlled swell and flow properties (rheology) by tailoring.

Bimodal polyethene (B) was polymerized with Ziegler-Natta type catalyst prepared according to WO 95/35323 in one loop and one gas phase reactor which are operated in series. Ethene was polymerized in presence of hydrogen in the loop resulting in MFR_2 = 363. Ethene was polymerized with 1-butene and hydrogen in the gas phase reactor. The production rate split of reactors was 45% / 55%. The final product MFR_{21} = 30 and density 957 kg/m^3. The polymerization results are presented in Table 1.

The powder from the above polymerization was compounded on Werner & Pfleiderer ZSK-30 extruder without and with peroxide addition. The peroxide was bis(tert.butylperoxyisopropyl)benzene (Perkadox 14S) and it was added as a master batch in the same powder. The master batch was made in a Pappenmeyer mixer. The compounding conditions were 200 rpm, 7 kg/h and Tm = 210°C.

The samples were tested by measuring MFR (by using standard ISO 1133), rheology and on Battenfeldt Fischer VK 1-4 blow molding line having screw diameter 50 mm and length 20 D by blowing 0.5 liter bottles. Rheometrics RDA II dynamic rheometer was used for rheological characterization. Measurements were made under nitrogen atmosphere at 190°C. In this way storage modulus (G'), loss modulus (G") and complex viscosity (η^*) were obtained as a function of complex modulus (G*). Shear thinning index SHIx/y was defined as the ratio of complex viscosities at a low G* value of x and at high G* value of y.

$$SHIx/y = \eta(x\ kPa) / \eta(y\ kPa)$$

The shear thinning index (SHI) measured at low shear and at high shear is used to describe the broadness of molecular weight distribution. The larger the SHI, the broader is the distribution.

The example shows the possibility to adjust the processability of bimodal polyolefin material on blow molding lines by molecular weight tailoring. The weight swell is an important parameter on blow molding lines. To have easy processability it has to be adjusted to a suitably low level. Tailoring gives a possibility to fine-tune, when necessary, the flow properties and weight swell, which is a function of die swell and

sagging. Tailoring decreases die swell and on the other hand the low zero shear rate viscosity results in less sagging and also slower rate of swelling.

Blow molding was done on a Battenfeldt Fischer VK 1-4 blow molding extruder having screw diameter 50 mm, length 20 D and 0.5 liter cylindrical bottle mold. Weight swell was measured by blowing the bottles with a constant (= same as reference) parrison length by adjusting the throughput.

The results are presented in Table 3.

	Test 1 (comparative)	Test 2
POKO 780 (w-%)	100	100
Pergadox 14S (ppm)	0	100
MFR_2	0.49	0.32
MFR_5	1.74	1.36
MFR_{21}	30.9	28.8
FRR 21/2	63.06	90.00
FRR 21/5	17.76	21.18
FRR 21/5 increase %		19
Mw *1000	170	
Mw/Mn	16.9	
MFR_5 decrease %		22
Bottle weight swell (%)	100	88.2
Viscosity (2.7 kPa)	24100	54500
SHI (2.7/210)	21.3	50.3
G' (5 kPa)	2090	3270

Example 3 (including comparative example)

The low content of stabilizer in the beginning of the extruder gives possibilities for tailoring reactions. The needed stabilizers for the end product can be fed in to the latter part of the extruder.

Bimodal polyethene (C) was polymerized with Ziegler-Natta type catalyst prepared according to WO 95/35323 in one loop and one gas phase reactor which are operated in series. The catalyst was prepolymerized before feeding into the loop reactor. The prepolymerization degree was 130 g/g. Ethene was polymerized in presence of hydrogen in the loop reactor resulting in MFR_2 = 545. Ethene was polymerized with 1-butene and hydrogen in the gas phase reactor. The production

rate split of loop and gas phase reactors was 42% / 58%. The final product MFR_{21} = 6.8 and density 945 kg/m^3.

Above described polymer was tailored during the melt homogenization step on Werner&Pfleiderer ZSK-70 twin screw extruder by feeding different amounts of Irganox B561 stabilizer with powder into the extruder and additionally by feeding 500 ppm Uvinul 2003 stabilizer into the latter part of the extruder. The feeding point of Uvinul was 14 * screw distance from the polymer feeding point. The total screw length of the extruder was 20 * screw diameter. Reference material was run without Uvinul 2003 feed. The compounding conditions were screw speed 250 rpm, T_m=275°C and output 260 kg/h.

The test materials were film blowed on Alpine film blowing line having 65 mm screw diameter. The used blow up ratio was 3.5. The neck height was 8 * die diameter and film thickness was 15 µm.

The example clearly shows improved bubble stability during film blowing and more balanced orientation which can be seen as better balance between machine direction (MD) and transverse direction tear strength (TD) for the film. The results are presented in Table 4.

Table 4

	Test #l	Test #2	Test #3	Reference
Irganox B561 feed	0 ppm	400 ppm	700 ppm	1500 ppm, w/o Uvinul
BUReff*	5.3	4.2	3.5	3.4
Bubble stability	excellent	excellent	some instability	fair
Dart drop ****	70 g	280 g	280 g	248
Tear strength (MD/TD)**	20/13 mN/µm	20/33 mN/µm	16/67 mN/µm	7/148

*) BUReff = Diameter of the bubble / Diameter of contracted neck

**) MD = machine direction, TD = transversal direction. Method = ISO 6383/2

***) Dart drop, ISO 7765-1

Example 4

Bimodal polyethene (D) was polymerized with said Ziegler-Natta type catalyst in one loop and one gas phase reactor which are operated in series. Ethene was

polymerized in presence of hydrogen in the loop reactor resufting in MFR_2 = 650. Ethene was polymerized with 1-butene and hydrogen in the gas phase. The production rate split of reactors was 47% / 53%. The final product MFR_{21} = 10.7 and density 947 kg/m^3.

Above described polymer was tailored during the melt homogenization step on Werner/ Pfleiderer ZSK-30 twin screw extruder by feeding different amounts of stabilizer Irganox 1500 with powder into the hopper before the extruder and additionally by feeding different amounts of Ronotec CF120 Vitamin-E stabilizer into the latter part of the extruder (barrel). The feeding point of Ronotec CF120 was was 24 * screw distance from the polymer feeding point. The total screw length of the extruder was 38 * screw diameter.

The evaluation of the samples was done by measuring MFR, rheology and by blowing film as described in the examples 1 and 2.

This example gives additional prove for the findings in example 3, and furthermore it shows the possibility to optimize tailoring degree with different stabilizer feeds.

Table 5

Polyethylene D/ZSK-30

	1 (comp.)	2	3	4	5
Tm (°C)	246	247	246	246	246
Ronotec CF120: ppm to barrel ppm to hopper		500	1000	500	500
Irg B215 (ppm)	1500			200	50
Visc. (2.7 kPa)	115000	293000	285000	183000	256000
SHI 2.7 kPa/210 kPa	38	89	88	58	79
Collin:					
Pressure	329	332	324	322	329
BUReff	3.2	4.3	4.3	3.7	4.2
Tear MD/TD	11/69	21/15	23/13	27/17	18/14
MFR_5	0.45	0.39	0.38	0.41	0.39
MFR_{21}	10.7	10.9	10.3	10.5	10.7
FRR 21/5	23.7	28.0	27.2	25.5	27.4
FRR 21/5 increase, %		18	15	8	16
MFR_5 decrease, %		13	16	9	13

Example 5

Bimodal polyethene (E) was polymerized with said Ziegler-Natta type catalyst in one loop and one gas phase reactor which are operated in series. The catalyst was prepolymerized before feeding into the loop reactor. The prepolymerization degree was 100 g/g. Ethene was polymerized in presence of hydrogen and 1-butene in the loop reactor resulting in MFR_2 = 540 and density 950 kg/m^3. Ethene was polymerized with 1-butene and hydrogen in the gas phase reactor. The production rate split of loop and gas phase reactors was 43% / 57%. The final product MFR_{21} = 25 and density 922 kg/m^3.

Above described polymer was tailored during the melt homogenization step on Werner&Pfleiderer ZSK-70 twin screw extruder by feeding 500 ppm Irganox B225 stabilizer with powder into the extruder and additionally by feeding 500 ppm or 900 ppm Ronotec CF-120 stabilizer into the latter part of the extruder. The feeding point of Ronotec was 14 * screw distance from the polymer feeding point. The total screw length of the extruder was 20 * screw diameter. Reference material was run without Ronotec CF 120 feed.

The test materials were film blowed on Reitenhauser film blowing line having 150 mm die diameter. The used blow up ratio was 3. The neck height was 8 * die diameter and film thickness was 25 µm.

The example clearly shows improved bubble stability during film blowing. The results are presented in Table 6.

Table 6

Ronotec	**500 ppm**	**900 ppm**	-
	Test #l	**Test #2**	**Test #3 reference**
Irganox B 225 feed	500 ppm	900 ppm	2500 ppm
BUReff*	3.8	3.5	2.7
Bubble stability	excellent	excellent	some instability

*) BUReff = Diameter of the bubble / Diameter of contracted neck

Table 1

Polymerization reaction conditions of examples 1-4

	Example 1	Example 2	Example 3	Example 4	Example 5	
Code	# 1	# 2	# 3	#4		
Temp. 1st reactor	95	95	95	95	85	°C
Temp. 2nd reactor	75	75	75	75	75	°C
Pressure, 1st reactor	65	65	61	65	81	bar
Pressure, 2nd reactor	20	20	20	20	20	bar
Ethene feed, 1st	33	26	32	29	31	kg/h
Ethene feed, 2nd	45	38	59	44	51	kg/h
1-butene feed, 1st	0	0	0	0	4.6	kg/h
1-butene feed, 2nd	4.7	0.9	6.1	2.7	20	kg/h
Hydrogen feed, 1st	35	31	87	49	76	g/h
Hydrogen feed, 2nd	7	51	29	19	4	g/h
MFR_2 after 1st	1030	363	545	650	540	g/10 min
Density after 1st	homopol.	homopol.	homopol.	homopol.	950	
MFR_{21} after 2nd	10.2	30	6.8	10.7	25	g/10 min
Density after 2nd	949	957	945	947	922	kg/m^3
Reactor split	47/53	44/56	42/58	47/53	43/57	%/%

Claims

1. Process for the preparation of an ethylene polymer product, containing from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α-olefin and having a broad molecular weight distribution, in which process:

(a) a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and at least a second ethylene polymer having a second average molecular weight which is higher than said first avarage molecular weight, and a second molecular weight distribution are formed into a blend having a third average molecular weight and a third molecular weight distribution which is at least bimodal;

(b) the blend of step (a) is heated and melt processed into a molten ethylene polymer having a fourth average molecular weight and fourth molecular weight distribution;

a stabilizer is optionally added in step (b), and

(c) the molten ethylene polymer is cooled and solidified into said ethylene polymer product,

characterized in that in step (b), the blend of step (a) is subjected to controlled free radical reactions so that the fourth average molecular weight is higher than, or approximately equal to, the third average molecular weight and the fourth molecular weight distribution is broader than the third at least bimodal molecular weight distribution.

2. Process according to claim 1, **characterized** in that the average molecular weights are measured and expressed as melt flow rates $MFR^i{}_m$, where i refers to said first, second, third and fourth average molecular weight, and m refers to the load of the piston used for measuring the MFRs, which load preferentially is 5.0 kg (m=5) (ISO 1133), the molecular weight distributions are expressed as the flow rate ratios, $FRR^i{}_{m1/m2}$, i.e. the ratios between high load MFR^is and low load MFR^is, where i refers to the first, second, third and fourth molecular weight distribution and m^1 and m^2 refer to the high load, preferentially 21.6 kg (subindex 21), and low load, preferentially 5.0 kg (subindex 5) or 2.16 kg, respectively.

3. Process according to claim 1 or 2, **characterized** in that in step (b), the blend of step (a) is subjected to free radical reactions so that the relative $MFR_{5.0}$ decrease, $-(MFR^4{}_5 - MFR^3{}_5):MFR^3{}_5$, is from 5 to 100%, preferentially from 10 to 80%.

4. Process according to claim 1, 2 or 3, **characterized** in that in step (b), the blend of step (a) is subjected to free radical reactions so that the relative broadening of the molecular weight distribution expressed as $+(FRR^4{}_{21/5} - FRR^3{}_{21/5}):FRR^3{}_{21/5}$ is from 5 to 100%, preferentially from 10 to 80%.

5. Process according to any preceding claim, **characterized** in that in step (b), the blend of step (a) is subjected to free radical reactions by means of initiator decomposition, such as photochemical bond cleavage, redox reactions and photochemical hydrogen abstractions, by means of γ-radiation, by means of electron beams or by means of thermal decomposition, preferentially by means of initiator decomposition by thermal bond cleavage, and/or by means of thermal treatment.

6. Process according to claim 5, **characterized** in that in step (b), the blend of step (a) is subjected to free radicals by means of thermal bond cleavage of one or several initiators chosen from azo initiators and peroxy initiators, preferentially peroxy initiators, most preferentially peroxy initiators, the 10 h half life temperature of which is from 38 to 172°C, preferentially 54 to 128°C.

7. Process according to claim 6, **characterized** in that in step (b), the peroxy initiators are chosen from; 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3; 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane; di(*tert*-butyl)peroxide; bis(*tert*-butylperoxy-isopropyl)benzene; *tert*-butylcumylperoxide; dicumylperoxide; 3,3,6,6,9,9-hexa-methyl-1,2,4,5-tetracyclononane; 4,4-di-t.-butylperoxy-n-butylvalerate; 1,1-di-*tert*-butylperoxycyclohexane; *tert*-butylperoxybenzoate; dibenzoyl peroxide; bis(2,4-di-chlorobenzoyl)peroxide; bis(p-chlorobenzoyl)peroxide; 2,2-bis(*tert*-butylperoxy)-butane; ethyl-3,3-bis(*tert*-butylperoxy)butyrate, preferentially 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane and bis(*tert*-butylperoxyisopropyl)benzene.

8. Process according to claim 6 or 7, **characterized** in that in step (b), the temperature is from 180°C to 260°C, preferentially from 190°C to 240°C.

9. Process according to claim 6, 7 or 8, **characterized** in that in step (b), the initial content of initiator or the initial content of initiator left after reaction with the optionally added stabilizer, is from 20 ppm to 2000 ppm, preferentially from 50 ppm to 500 ppm, calculated on the weight of the blend of step (a).

10. Process according to one of claims 6 to 9, **characterized** in that in step (b), the average heating and melt processing time is from 0.5 min. to 30 min., preferentially from 0.5 min. to 10 min.

11. Process according to claim 5, **characterized** in that in step (b), the blend of step (a) is subjected to free radical reactions by means of thermal treatment.

12. Process according to claim 11, **characterized** in that in step (b), the temperature is from 220°C to 320°C, preferentially from 240°C to 300°C.

13. Process according to claim 11 or 12, **characterized** in that in step (b), the average heating and melt processing time is from 0.1 min. to 30 min., preferentially from 0.5 min. to 10 min.

14. Process according to one of claims 5 to 13, **characterized** in that in step (b), an essentially unstabilized or slightly stabilized blend of step (a) is used, whereby preferentially at the end of step (b), after the radical reactions have taken place, a stabilizing amount of stabilizer is added to the molten ethylene polymer.

15. Process according to one of claims 11 to 14, **characterized** in that in step (b), from 0 to 500 ppm of a first stabilizer is added to the blend of step (a) essentially at the beginning of step (b), and from 400 to 1400 ppm of a second stabilizer is added to the molten ethylene polymer essentially at the end of step (b), the first and second stabilizers being equal or different.

16. Process according to claim 15, **characterized** in that in step (b), the first stabilizer is a different stabilizer than the second stabilizer, preferentially so that the first stabilizer is a weak process stabilizer allowing radical reactions partially, whereas the second stabilizer is a strong process stabilizer essentially preventing radical reactions during melt processing.

17. Process according to any preceding claim, **characterized** in that in step (a), the blend is formed by mixing the first ethylene polymer and at least the second ethylene polymer.

18. Process according to claim 17, **characterized** in that in step (a), the ratio between the first ethylene polymer and the second ethylene polymer is between 20:80 and 80:20, preferentially between 20:80 and 60:40.

19. Process according to claim 17 or 18, **characterized** in that in step (a), the melt flow ratio $MFR^1{}_2$ of the first ethylene polymer is from 50 to 2000 g/10 min, preferentially from 100 to 1500 g/10 min.

20. Process according to claim 17, 18 or 19, **characterized** in that in step (a), the melt flow ratio·$MFR^{2,\ etc.}{}_{21}$ of at least the second polymer is from 0.05 to 50 g/10 min., preferentially from 0.10 to 20 g/10 min.

21. Process according to any of claims 17 to 20, **characterized** in that in step (a), the first ethylene polymer has a C_3-C_{10} α-olefin repeating unit content of from 0.0 to 10% by weight, of the first ethylene polymer.

22. Process according to any of claims 17 to 21, **characterized** in that in step (a), at least the second ethylene polymer has a C_3-C_{10} α-olefin, preferentially 1-butene or 1-hexene, repeating unit content of from 1.0 to 25% by weight, preferentially from 2.0 to 15% by weight, of at least the second ethylene polymer.

23. Process according to any of claims 17 to 22, **characterized** in that in step (a), the proportion of the first ethylene polymer and the second ethylene polymer, the MFR^1 and MFR^2 of said ethylene polymers and the C_3-C_{10} α-olefin repeating unit content of said ethylene polymers are such that the $MFR^3{}_{21}$ of the blend of step (a) is between 5 and 50 g/10 min., the C_3-C_{10} α-olefin repeating unit content of the blend of step (a) is from 0.2 to 20% by weight, preferentially 0.5-15% by weight, and the $FRR^3{}_{21/5}$ is between 10 and 40, preferentially so, that after step (b), the fourth molecular weight distribution is at least bimodal.

24. Process according to one of claims 1 to 16, **characterized** in that in step (a), the blend of step (a) is formed by a polymerization process comprising several substeps in which the first ethylene polymer is prepared by polymerizing in a substep (a_1), the second ethylene polymer is prepared by polymerizing in a substep (a_2), optional further ethylene polymers are prepared by polymerizing in optional further substeps, whereby the ethylene polymer of each step is present in the following step.

25. Process according to claim 24, **characterized** in that in substep (a_1) and/or substep (a_2), a catalyst system based on at least a tetravalent titanium compound as procatalyst and an organoaluminium compound as cocatalyst, preferentially based on titanium tetrachloride $TiCl_4$, magnesium chloride $MgCl_2$, an optional inert

carrier and/or an optional electron donor compound as procatalyst, as well as a trialkylaluminium as a cocatalyst, is used.

26. Process according to claim 24 or 25, **characterized** in that the catalyst system is added to the first substep (a_1) and the same catalyst system is used in the second and optional additional substeps.

27. Process according to any of claims 24 to 26, **characterized** in that in substep (a_1), a hydrogen amount is used, leading to a melt index $MFR^1{}_{21}$ of the first ethylene polymer of from 50 to 2000 g/10 min., preferentially from 200 to 1500 g/10 min., if substep (a_1) is performed first.

28. Process according to any of claims 24 to 27, **characterized** in that in substep (a_1), no or little C_3-C_{10} α-olefin is used so that the first ethylene polymer has a C_3-C_{10} α-olefin repeating unit content of 0.0 to 10.0% by weight, of the first ethylene polymer.

29. Process according to any of claims 24 to 28, **characterized** in that in substep (a_2) and further optional substeps, so much C_3-C_{10} α-olefin is used that at least the second ethylene polymer has a C_3-C_{10} α-olefin, preferentially 1-butene or 1-hexene, repeating unit content of from 1.0 to 25% by weight, preferentially from 2.0 to 15.0% by weight, of at least the second ethylene polymer.

30. Process according to any of claims 24 to 29, **characterized** in that in step (a), the ratio between the first ethylene polymer and the second ethylene polymer is between 20:80 and 80:20, preferentially between 20:80 and 60:40.

31. Process according to any of claims 24 to 30, **characterized** in that in substeps (a_1) and (a_2), said reaction temperature, catalyst system, portions of C_3-C_{10} α-olefin, amount of hydrogen, and ratio between the first olefin polymer and the second olefin polymer produced, are regulated so that the $MFR^3{}_{21}$ of the blend of step (a) is between 5 and 50 g/10 min., the C_3-C_{10} α-olefin repeating unit content of the blend of step (a) is from 0.2 to 20% by weight, preferentially from 0.5 to 15.0% by weight, and the $FRR^3{}_{21/5}$ is between 10 and 40, preferentially so, that after step (b), the fourth molecular weight distribution is at least bimodal.

32. Ethylene polymer product, preferentially a film product, containing from 0.0 to 20% by weight of repeating units of a C_3-C_{10} α-olefin and having a broad

molecular weight distribution, **characterized** in that it has been prepared by a process according to one of claims 1-31.

33. The use of the ethylene polymer product according to claim 32 or prepared according to one of claims 1 to 31 for extrusion applications, especially film blowing, cast-line extrusion, pipe coating, extrusion coating, and in blow moulding applications.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 97/00353

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04, C08F 10/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	File WPI, Derwent accesion no. 94-086089, MITSUBISHI PETROCHEMICAL CO LTD: "Polyethylene resin compsn. prodn., for high speed inflation - by kneading compsn. contg. low and high mol. wt. polyethylene"; & JP,A,6009788, 940118, abstract --	1,5-8,17, 32-33
X	EP 0404552 A2 (MOBIL OIL CORPORATION), 27 December 1990 (27.12.90), abstract; page 4, lines 30-35; claims 1-8 --	1,5-8,17, 32-33
X	US 5405917 A (FRANCIS X. MUELLER, JR. ET AL), 11 April 1995 (11.04.95), abstract; claims 1-3, 16; column 4, lines 46-50 --	1,5-9,32-33

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 Sept 1997	09-09- 1997
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Agneta Österman Wallin Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 97/00353

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	File WPI, Derwent accession no. 89-361152, NIPPON PETROCHEMICALS CO LTD: "Ethyleneå-type polymer compsn. for blow moulding - comprises blend of high mol. wt. and low mol. wt. ethyleneå type polymers together with fee radical polymerisation initiator"; & JP,A,1271441, 891030, the whole abstract	1-33

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INTERNATIONAL SEARCH REPORT

Information on patent family members

06/08/97

International application No.
PCT/FI 97/00353

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0404552 A2	27/12/90	CA 2019164 A JP 3074447 A US 5073598 A	21/12/90 29/03/91 17/12/91
US 5405917 A	11/04/95	NONE	